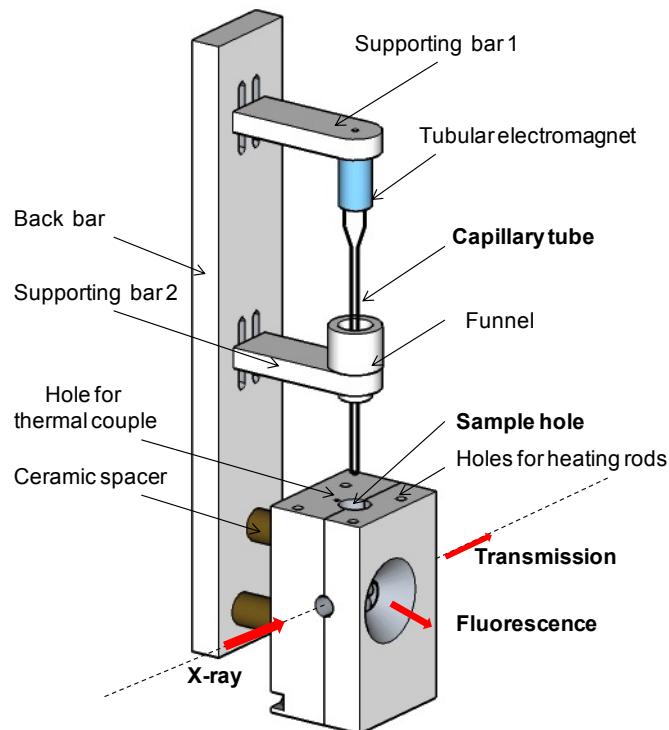


Supporting Information

A Metal-Cluster-Based Heterogeneous Catalyst for Homogeneous Catalytic Reactions: XAS and Reaction Kinetic Studies of their Activity and Stability against Leaching

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Scheme S1. The reactor used in *in situ* XAS measurement. The heating block was adapted from a design given in a previous publication.¹ For *in situ* experiments, the capillary tube reactor is initially held above the heating block by a tubular electromagnet. After ramping the heating block to a given reaction temperature, the capillary can be dropped into the sample hole by turning off the electromagnet.

Table S1. EXAFS fitting parameters and R-factors. The error bars are given in parenthesis. CN_{Pt-Pt} , CN_{Pt-Cl} and CN_{Pt-O} are the Pt coordination numbers to Pt, Cl, and O, respectively. R_{Pt-Pt} , R_{Pt-Cl} , and R_{Pt-O} are the Pt-Pt, Pt-Cl, and R-O distances, respectively.

	Reduction 1	Oxidation 1	Reduction 2	Oxidation 2
CN_{Pt-Pt}	5.0 (0.5)	0.9 (0.1)	4.4 (0.4)	0.3 (0.1)
CN_{Pt-Cl}	0.3 (0.2)	2.0 (0.2)	0.6 (0.1)	2.6 (0.3)
CN_{Pt-O}	0.9 (0.4)	0.75 (0.2)	0.79 (0.2)	0.52 (0.2)
R_{Pt-Pt} (Å)	2.745 (0.004)	2.769 (0.005)	2.743 (0.003)	2.781 (0.01)
R_{Pt-Cl} (Å)	2.201 (0.034)	2.318 (0.004)	2.302 (0.014)	2.321 (0.005)
R_{Pt-O} (Å)	1.969 (0.025)	1.997 (0.017)	1.974 (0.021)	2.037 (0.033)
E_0 (eV)	4.6 (1.1)	10.8 (1.0)	6.2 (0.9)	13.85 (1.0)
σ (Å ²)	0.0062 (0.0004)	0.0035 (0.0005)	0.0065 (0.0004)	0.0021 (0.0006)
R-factor	0.0064	0.0064	0.0051	0.0049

Table S2. The NEXAFS fitting parameters and R-factors for Oxidation 1, Reduction 2, and Oxidation 2 smaples. Error bars are given in parenthesis.

Reference Compound	Oxidation 1	Reduction 2	Oxidation 2
Reduction 1	0.53 (0.01)	0.80 (0.01)	0.28 (0.02)
Zeise's Pt dimer	0.19 (0.01)	NA	0.23 (0.02)
K ₂ PtCl ₄	NA	0.20 (0.01)	NA
H ₂ PtCl ₆	0.28 (0.02)	NA	0.49 (0.02)
E_0 (eV)	0.11 (0.01)	0.03 (0.01)	0.07 (0.01)
R-factor	2.5E-05	3.0E-05	3.4E-05

Table S3 the NEXAFS fitting parameters and R-factors for a pre-oxidized sample during the reaction condition without PhICl₂. Error bars are given in parenthesis. Zeise's Pt dimer and H₂PtCl₆ are used as the reference compounds for Pt(II) and Pt(IV) species, respectively.

	Before reaction	15 min	30 min	60 min	90 min	150 min	335 min	950 min	after reaction
Pt(0)	46 (2)	43 (2)	42 (2)	46 (3)	45 (3)	47 (3)	51 (3)	52 (3)	53 (3)
Pt(II)	31 (2)	37 (2)	40 (2)	40 (3)	42 (3)	43 (3)	42 (3)	43 (3)	39 (3)
Pt(IV)	24 (3)	20 (3)	18 (3)	14 (4)	13 (4)	11 (4)	7 (4)	5 (4)	8 (4)
R-factor	3.7E-5	3.8E-5	3.5E-5	4.5E-5	4.3E-5	4.7E-5	5.3E-5	6.6E-5	4.6E-5

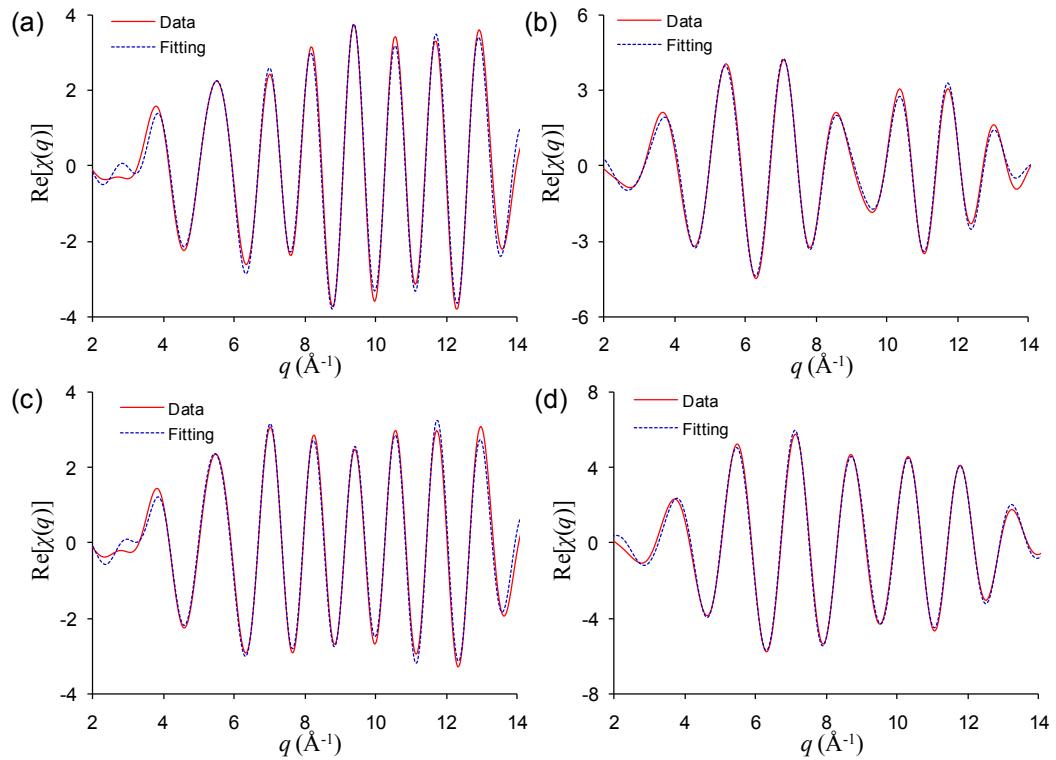


Figure S1. EXAFS spectra and the fitting in q space for (a) Reduction 1, (b) Oxidation 1, (c) Reduction 2, and (d) Oxidation 2 samples.

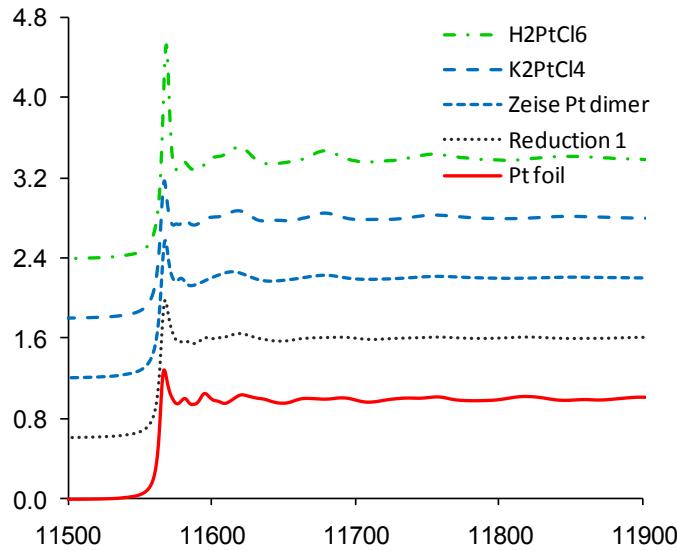


Figure S2. NEXAFS of standard compounds: Reduction 1 for Pt(0) species, Zeise Pt dimer, and K_2PtCl_4 for Pt(II) species, and H_2PtCl_6 for Pt(IV) species. The spectrum of Pt foil is also given for comparison.

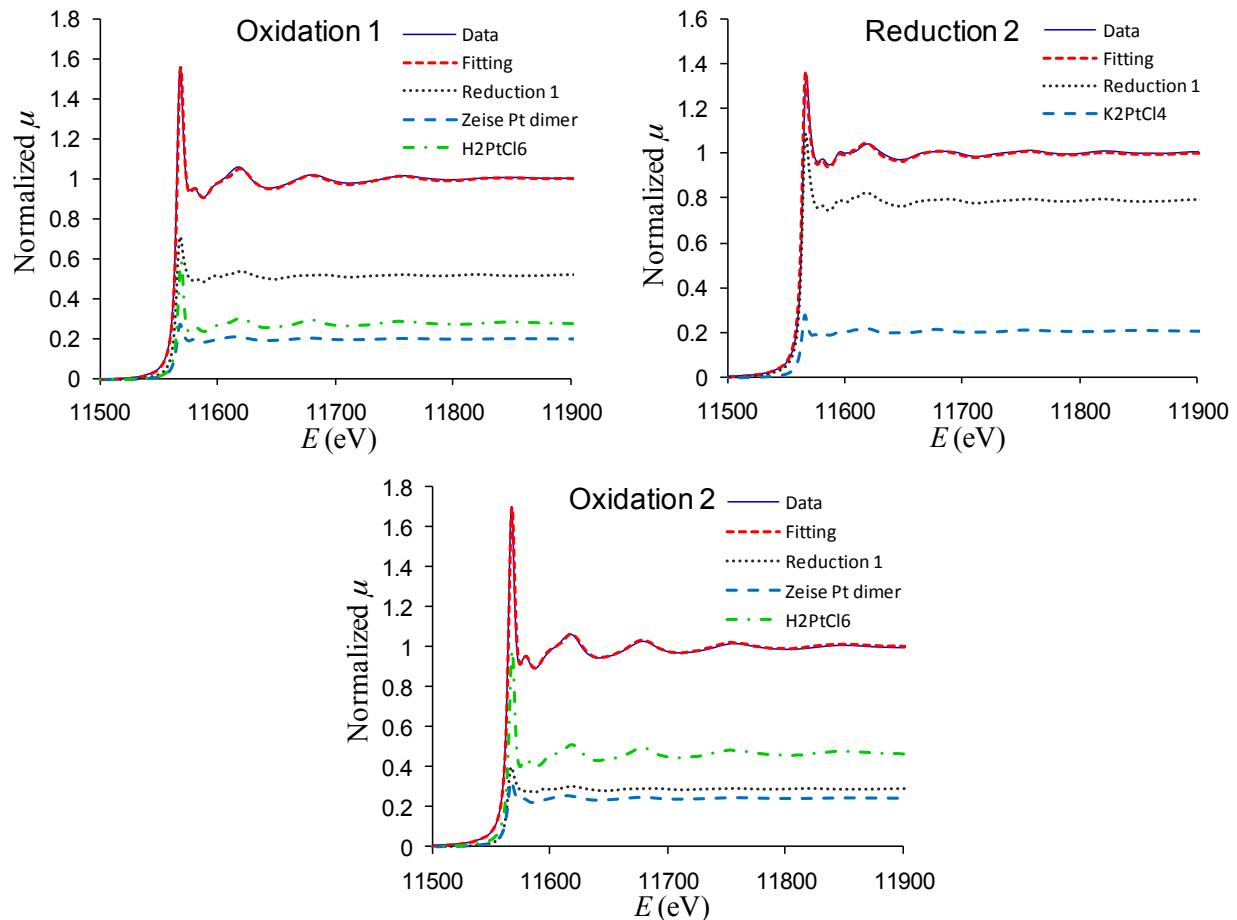


Figure S3. NEXAFS fits of Oxidation 1, Reduction 2, Oxidation 2 samples. The energy range of fitting is from -50 eV to 300 eV with respect to the edge energy. The edge energy shift and the post-edge slope are allowed to vary in the linear combination fitting.

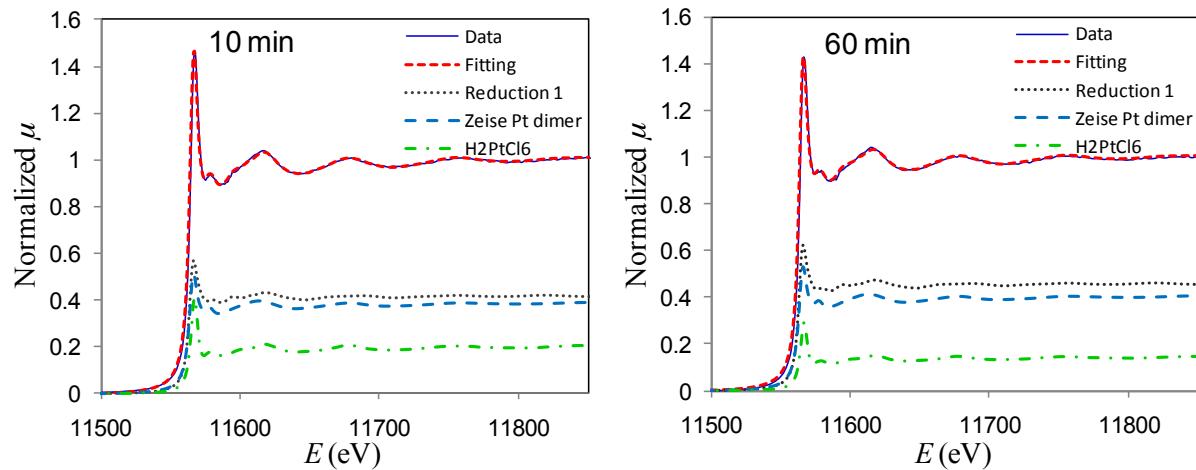


Figure S4. Representative fits of the NEXAFS spectra under reaction conditions. The energy range of fitting is from -50 eV to 300 eV with respect to the edge energy. The edge energy shift and the post-edge slope are allowed to vary in the linear combination fitting.

References

- ¹ B. R. Fingland, F. H. Ribeiro, and J. T. Miller. *Catal. Lett.*, 131, 1 (2009).